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13. ABSTRACT (Maximum 200 words)

Report developed under STTR contract for topic ARMY02-T010. The magnetic resonance force microscope is an exciting powerful new technology for detecting nuclear magnetic and electron-spin resonance of nanoscale samples and imaging subsurface features. The feasibility of producing a novel commercially viable magnetic resonance force microscope (MRFM) has successfully been demonstrated.

Key technologies required to bring the instrument to market with sensitivity to a few thousand protons were demonstrated, including a novel cryogenic coarse approach mechanism and the first-ever batch fabrication of attoNewton-sensitive "ultrafloppy" cantilevers with individual nanomagnets on the tips.

A prototype digital-signal-processor (DSP) based cantilever controller suitable for use in an MRFM instrument was developed. It is a significant accomplishment to be able to employ a DSP in a scanned probe microscope measurement.

We have determined that this technology is suitable for optimization and manufacture of a commercial microscope, with initial applications in thin-film materials analysis. Eventual broad commercial and military applications will benefit from this technology including: research of advanced materials, advanced semiconductor-device research (e.g. individual impurity and defect characterization, assaying spin injection in spintronics devices), single-molecule analytical chemistry, infectious disease research, biotechnology, nanoelectronics, and new solid-state physics research.

14. SUBJECT TERMS

STTR Report: Magnetic resonance force microscope, nuclear magnetic resonance, magnetic Resonance imaging, electron spin resonance, cryogenic atomic force microscope, model-based control, real-time control, embedded control.

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Summary

The magnetic resonance force microscope is an exciting powerful new technology for detecting nuclear magnetic and electron-spin resonance of nanoscale samples and imaging subsurface features. This Small Business Technology Transfer Research Phase I project has successfully demonstrated the feasibility of producing a novel commercially viable magnetic resonance force microscope (MRFM).

Building on an already successful Cornell prototype magnetic resonance force microscope, we have demonstrated additional key technologies required to bring the instrument to market with sensitivity to a few thousand protons. Demonstrated technologies include a novel cryogenic coarse approach mechanism and the first-ever batch fabrication of attoNewton-sensitive "ultrafloppy" cantilevers with individual nanomagnets on the tips. A next-generation scanning MRFM microscope, capable of detecting NMR from $\sim 10^4$-10^5 protons, has been built at Cornell and control experiments have been carried out showing feasibility. We have determined that the microscope is suitable for optimization and manufacture by CryoIndustries.

The main focus of this Phase I project has been a close collaboration between SC Solutions and Cornell University in which we have developed a prototype digital-signal-processor (DSP) based cantilever controller suitable for use in an MRFM instrument. MRFM experiments require operating a fragile ultrafloppy cantilever near a surface, where surface-cantilever interaction forces lead to deleterious changes in cantilever resonance frequency. These shifts are large compared to the width of the cantilever's mechanical resonance. Since all proposed MRFM experiments require a resonant driving of the cantilever, actively tracking the cantilever frequency near a surface is an essential component of a commercial MRFM instrument. A DSP controller is also needed in MRFM experiments to actively damp cantilever thermomechanical position fluctuations during image encoding. Using a combination of cantilever data from Cornell atomic force and magnetic resonance force microscopes and computer simulations, SC Solutions has examined a number of candidate frequency-tracking DSP algorithms, found one that is suitable for further optimization, and designed hardware suitable for implementing the algorithm. This is a significant accomplishment, because, to our knowledge, only one other group worldwide has attempted to employ a DSP in a scanned probe microscope measurement.

Keywords

Magnetic resonance force microscope, nuclear magnetic resonance, magnetic resonance imaging, electron spin resonance, cryogenic atomic force microscope, model-based control, real-time control, embedded control.

Potential markets

Since MRFM enables imaging of subsurface features for the first time and has the unique capacity of being able to image with isotopic selectivity, the potential commercial applications are enormous. CryoIndustries envisions producing a cryogenic atomic force / magnetic resonance force microscope for initial applications in thin-film materials analysis. The technology will have eventual broad commercial and military utility including: research of advanced materials, advanced semiconductor-device research (e.g. individual impurity and defect characterization, assaying spin injection in spintronics devices), single-molecule analytical chemistry, infectious disease research, biotechnology, nanoelectronics, and new solid-state physics research (e.g. investigations of electron spin coupling mechanisms and quantum computational physics).

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Project Objectives

The primary objective of the Phase I project was to develop a commercially feasible design for a magnetic resonance force microscope capable of detecting a single electron spin or a few thousand nuclear spins, and to carry out experiments to show that building such an instrument is feasible. In our Phase I proposal, we identified four tasks to be carried out to reach this objective:

1. Integrate three-dimensional scanning into Cornell's existing magnetic resonance force microscope. This capability builds on Cornell's demonstrated cryogenic atomic force microscope probe head.

2. Batch fabricate ultrafloppy Si microcantilevers with integral nanomagnet tips.

3. Design and begin testing a dual-use digital-signal-processor-based feedback controller. The controller will be capable of a) actively damping thermomechanical motions in an ultrafloppy silicon microcantilever, as required to detect single-spin magnetic resonance, and b) actively control large-amplitude cantilever motions, as required to perform atomic force microscopy with ultrafloppy cantilevers.

4. Demonstrate the feasibility of developing a magnetic resonance force microscope with sufficient sensitivity for detecting one electron magnetic moment or less than one thousand proton magnetic moments in a one hertz bandwidth.

We have made substantial and dramatic progress on all these tasks. At the end of Phase I, we now have all major components in place for CryoIndustries to begin designing and testing a commercially viable magnetic resonance force microscope capable of detecting a few thousand nuclear spins.

Work Carried Out

A new approach to detecting magnetic resonance with cantilevers

As we began this project, the Cornell team identified two extremely serious potential problems that could frustrate bringing magnetic resonance force microscopy (MRFM) to market, and invented a novel variant of MRFM that avoids these potential problems. In this section we introduce the new approach. Fortuitously, the approach requires improving nearly the same technologies detailed in our Phase I STTR proposal. We are very proud of this new method for detecting magnetic resonance with a cantilever and think that it significantly improves our chances of seeing a single nuclear spin in the near future with a commercially viable apparatus.

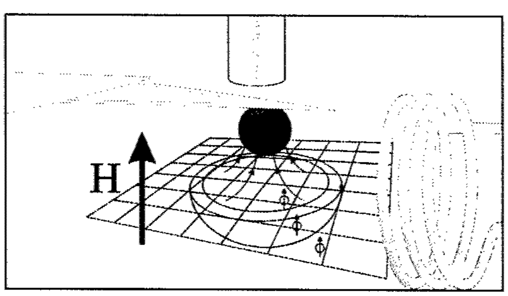


Figure 1. The magnetic resonance force microscope concept.

In order to understand the advantages of the new approach, first recall how MRFM works. The magnetic resonance force microscope (MRFM) concept [1– 4] is illustrated in the above cartoon. A magnetic-tipped cantilever is brought close to a sample surface containing spins to be studied. The spins can be unpaired electron spins or nuclear spins, e.g., hydrogen nuclei. Next, radiofrequency (RF) irradiation produced by a coil is applied to the sample. The RF interacts most strongly with spins in a constant-field "sensitive slice" where the magnetic-field induced spin energy level splitting equals the energy of the RF irradiation (the magnetic resonance condition). The RF is frequency modulated in such a way that the spins in the sensitive slice are cyclically inverted at the cantilever's mechanical resonance frequency (~few kHz). This drives the cantilever into oscillation (~few nanometers amplitude) via the gradient-dipole force acting between sample spins and the magnetic particle at the end of the cantilever. The cantilever oscillation is typically registered with an optical fiber interferometer. The amplitude of the oscillation is proportional to the number of spins under the tip in the sensitive slice.

The MRFM concept as just described has to two serious problems that could prevent it being used commercially to study materials of interest. First, it requires modulating sample magnetization for 100's of milliseconds to observe signal. It is expected that most (biological/polymer) samples of interest will not have favorably long $T_{1\rho}$ nuclear magnetic relaxation times at cryogenic temperatures where MRFM is most sensitive. Second, using fragile ultrasensitive cantilevers in the geometry shown in the MRFM cartoon above is problematic. To avoid "snapping in" to the surface due to van der Waals forces, the cantilever should approach the surface in a perpendicular orientation. In the perpendicular orientation, however, the net force is *zero* for a magnetic tipped cantilever interacting with a uniform sample of spins below, by symmetry.

The figure below shows our novel approach to detecting nuclear magnetic resonance with a magnetic tipped cantilever that avoids these potentially serious problems.

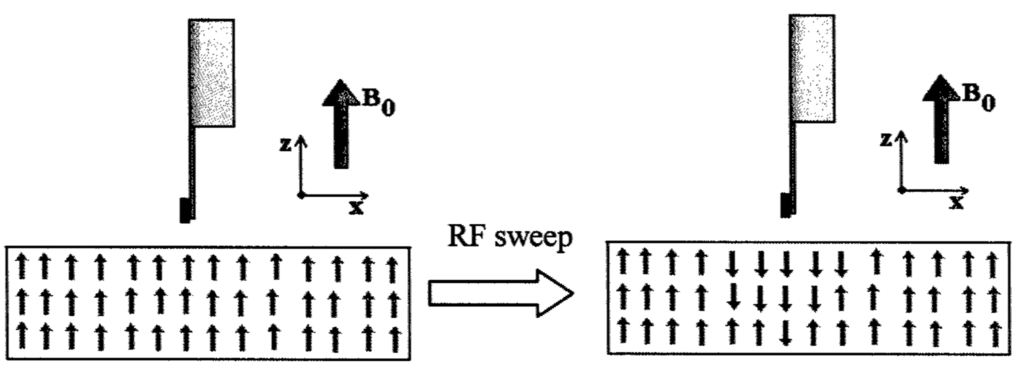


Figure 2. Protocol for detecting magnetic resonance as a change in the cantilever spring constant.

In the new approach a magnetic tipped cantilever approaches the surface in the favorable perpendicular orientation. An RF frequency sweep is applied once to flip the spins in a bowl below the sample. There is now a tiny preference for the cantilever to want to lie over the inverted bowl of spins. This will be registered in a tiny change in the spring constant of the cantilever, which we will record as a shift in the resonance frequency of the cantilever.

Approaching the surface in the perpendicular orientation is clearly compatible with using the most fragile ultrasensitive silicon cantilevers. Another advantage of our approach is that the spins are only flipped once. The change in spring constant is recorded for a time T_1, the spin-lattice relaxation time, which is typically much longer than the time $T_{1\rho}$ that spins can be coherently flipped (as in the conventional MRFM experiment). Our new approach has a signal-to-noise advantage over MRFM of $(T_1 / T_{1\rho})^{1/2}$ which we expect can easily be > 100 for biological solids and polymers at low temperature.

Numerical estimates indicate that employing our first batch of submicron-scale magnets, shown below in Task 2, will lead to spring constant change from a polystyrene sample at 4 Kelvin and 9 Tesla is approximately a nanoNewton/meter. For the micron scale tips also shown below, the signal is approximately ten times larger. If is feasible to detect spring constant changes of this magnitude with the ultrasensitive cantilevers shown below. With the available signal to noise, we can expect to achieve an imaging resolution of ~100 nanometers with the technology reported below. A detailed article describing signal-to-noise calculations, numerical simulations, and scaling laws for spring constant detection of magnetic resonance is in preparation.

Improving the per-spin signal to noise ratio in the new spring constant detection experiment requires the optimizing same technologies as with force detection: (1) Task 1 Build a probe in which a cantilever can approach a surface at cryogenic temperatures and radiofrequency irradiation can be applied to the sample spins. (2) Task 2 Employ thin, long, narrow cantilevers for highest force sensitivity, fabricate nanoscale magnetic tips to maximize the interaction of the tip with sample spins, and work at cryogenic temperatures to minimize thermomechanical fluctuations in the cantilevers (Task 2), (3) Task 3 Drive the cantilever on resonance. Using spring constant detection to observe single proton magnetic resonance will be considered in the Task 4 work description.

In force detection, following the cantilever frequency is required to keep the sample spin modulation on resonance with the cantilever. With spring constant detection of magnetic resonance, although we longer need to drive the sample spins other than flipping them once, we will want to drive to cantilever at resonance (for example, capacitively with a drive wire) in order to read out its frequency accurately. For spring constant detection, we need to detect very small cantilever resonance shifts (milliHertz) and on a relatively fast time scale (10's of milliseconds). Although the approach of detecting magnetic resonance as a change in cantilever spring constant has many advantages, measuring the required small transient frequency shifts is very challenging, and so Task 3 has been our major focus.

Task 1: A scanning magnetic resonance force microscope

Task 1 was carried out at Cornell University, in consultation with CryoIndustries.

The starting point

In our Phase I proposal, we showed a prototype magnetic resonance force microscope that we used to detect both electron spin resonance at 77 Kelvin and nuclear magnetic resonance at room temperature. In these preliminary experiments, micron scale samples were glued to commercial cantilevers. The prototype apparatus was of limited commercial interest because 1) it required gluing samples to the tips of fragile atomic force microscope cantilevers, and 2) we were unable to scan the sample and record images. A photograph of the prototype apparatus is included in Figure 3, for comparison to the improved Phase I MRFM probe to be described shortly.

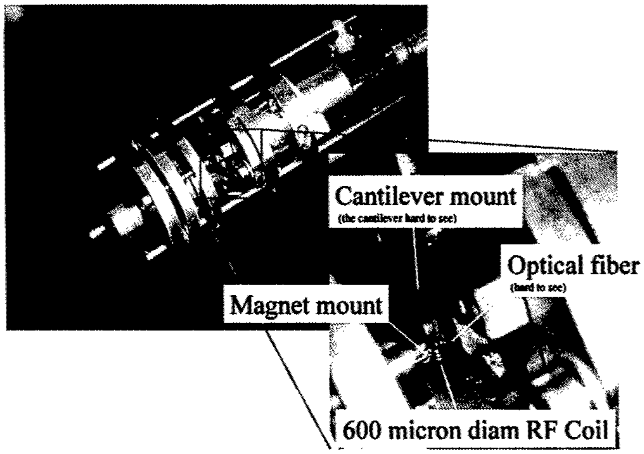


Figure 3. The Cornell prototype magnetic resonance force microscope. This microscope had been developed before the start of the STTR work.

Cryogenic scanning

Our goal in Task 1 was to design a magnetic resonance force microscope in which a magnetic tipped cantilever could be brought close to a surface at cryogenic temperatures and scanned in *x*, *y*, and *z* to record a nuclear magnetic resonance image. Figure 4 shows the MRFM probe that we have developed in Phase I to meet these criteria.

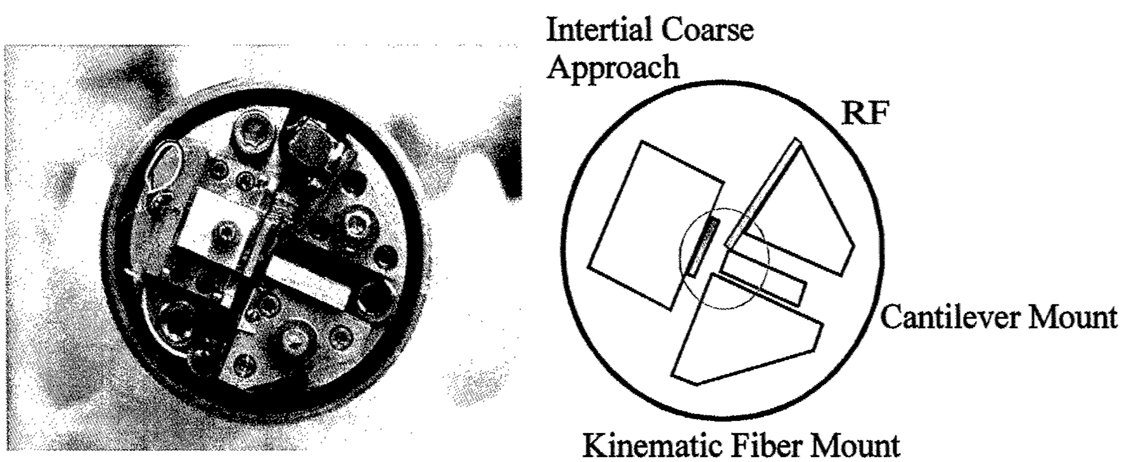


Figure 4. The magnetic resonance force microscope developed during this Phase I STTR grant. The central innovation in the Phase I MRFM probe is that it now includes a novel slip-stick inertial coarse approach mechanism that is based upon a design previously developed by Silveira and Marohn at Cornell for work down to 4 Kelvin. See Reference 5. This approach mechanism allows us to step the cantilever towards a sample surface in electrically controllable nanometer-size steps.

We have used the coarse approach mechanism to examine the behavior of an ultrafloppy cantilever brought within ~10 nm of a polystyrene surface at 77 Kelvin. The data appears below in the Task 2 work summary. So far, we find that the coarse approach mechanism behaves well down to only ~50 K. This was somewhat surprising given our success at designing and using a similar 4-Kelvin mechanism. Given our experience in this area, we are confident that with a few

more weeks of optimization, it will be straightforward to make the probe work more reliably at 4 Kelvin as desired.

In Phase I we have implemented and tested a number of other probe innovations that will help make the probe more commercially viable. In the previously developed Cornell MRFM prototype probe, a displacement-measuring optical fiber was positioned with respect to the cantilever with an optical microscope and then glued permanently in place at room temperature. In the Phase I MRFM probe, we have separated the cantilever mounting and fiber stages. This allows more control over fiber positioning and makes it easy to add a wire near the fiber to capacitively drive the cantilever. More importantly, it allows us to quickly (~1-2 hours) interchange cantilevers, which is crucial since we are still gaining experience in handling ultrafloppy cantilevers without the breaking them due to static electricity or mishandling. Finally, the Phase I MRFM probe includes *xyz* positioning capability on the radiofrequency coil. The *xyz* stages are custom-designed kinematic mounts which offer a precision of ~5 microns; our tests show that the stages maintain alignment well upon cooling to liquid helium temperatures. Considerable attention has been devoted to designing the RF coil probe circuitry, which we will now detail.

Radiofrequency coil

Figure 5 below shows the radiofrequency circuit used in the Cornell prototype MRFM probe, which operated at ~300 MHz. In order to save space, variable tuning and matching capacitors were located some centimeters at the end of a half wave line. Experiments shown at below left indicate that the RF magnetic field that results from this tank circuit is dangerously low for MRFM work.

A pulsed nuclear magnetic resonance (NMR) experiment was carried out with the Cornell prototype MRFM probe to accurately calibrate the RF field strength. Here we used an RF pulse to evolve the sample's nuclear magnetization away from the static field, waited for a some time for transverse magnetization to dephase, and then read out the remaining longitudinal magnetization with a frequency sweep that flipped the nuclear magnetization to excite the cantilever. The resulting cantilever force is shown at the right as a function of the pulse time, and shows the expected cosinusoidal evolution. From evolution frequency we can estimate that we are only delivering ~5 Gauss of transverse field for ~1 Watt of RF applied to the tank circuit. This is below what is required for solid-state NMR, and is attributed to our use of a very tiny coil in conjunction with a large quarter wave cable.

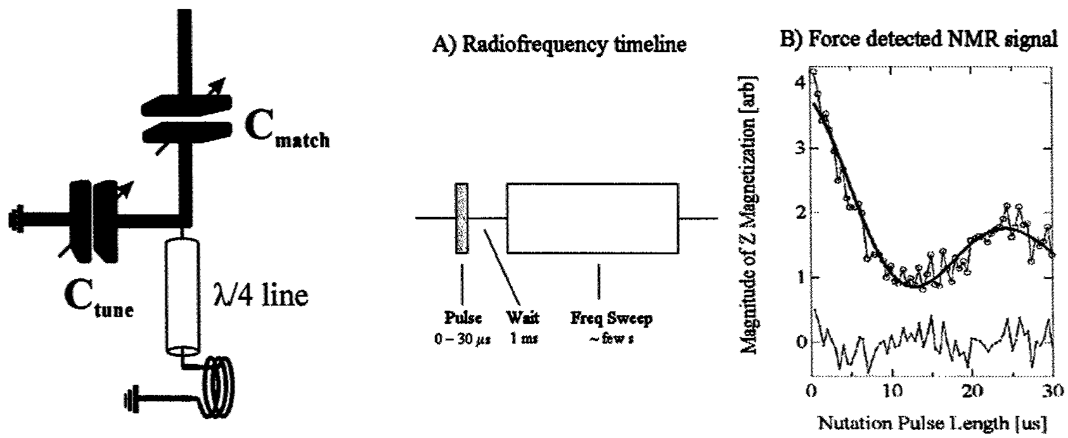


Figure 5. Left: The RF tank circuit used in the Cornell prototype MRFM probe. Right: Calibrating the RF field strength using force detection of pulsed NMR.

In the Phase I MRFM probe we have placed the whole RF tank circuit on an approximately one inch square PCB board, sketched in Figure 6. We did this to eliminate the quarter wave line and to minimize stray inductances and capacitances. We expect to obtain up to ~20 Gauss of transverse fied at ~1 Watt with this approach. The design in borrowed from the Pennington group at Ohio State who use it in microcoil NMR experiments at room temperature. (They have only used the circuit at room temperature.) While we have not used this tank circuit in a pulsed NMR experiment yet, the RF reflectance curve shown below indicates that we are able to obtain to well-matched coil resonance at 4 Kelvin using the PCB design, which is very promising.

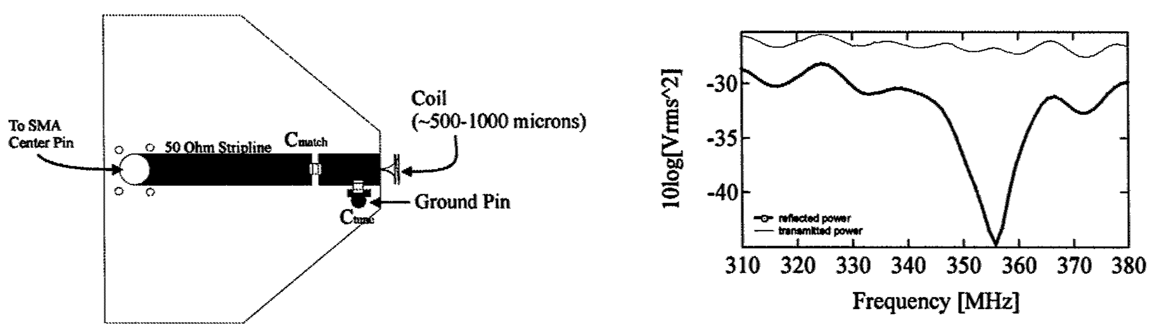


Figure 6. Left: The PCB board containing an RF microcoil and miniature tank circuit constructed for the Phase I MRFM probe. Right: Circuit reflectivity showing a high Q circuit.

The viability of commercial prototyping and production

On January 20th, George Svenconis of CryoIndustries visited the Marohn laboratory at Cornell to consult on cryogenic probe design and to assess his company's ability to reproduce the Cornell Phase I probe described above upon start of the Phase II STTR project. A number of topics were discussed including how to best achieve variable temperature operation and vibration isolation. The conclusion was reached that prototyping the next-generation MRFM probe is well within CryoIndustries' machining capabilities and well suited to their expertise in working with stainless steel for cryogenic applications.

Another insight that came from the meeting is that a profitable way to bring the MRFM probe to market might be to start with selling a simplified design capable of variable temperature atomic

force microscopy. This would get CryoIndustries into the scan probe microscope market with a product that can be produced immediately. Only one other company, RHK, currently manufactures a cryogenic atomic force microscope, and they are a German company.

Task 2: Batch fabricating ultrafloppy cantilevers with nanomagnet tips

Task 2 was carried out at Cornell University, making use of the unique world-class facilities available at the NSF-subsidized Cornell Nanofabrication Center.

Fabrication and characterization

We have learned how to batch fabricate, for the first time, ultrafloppy silicon microcantilevers with integral magnetic tips. We are the first group worldwide to be able to do this and it marks a major step towards making MRFM commercially viable. Up until now all MRFM tips have been prepared one at a time by hand, which is tedious and unreliable. We are also pleased to report that we have been able to characterize the magnetic properties of the submicron magnetic particles using frequency-shift cantilever magnetometry. Finally, we have carried out control experiments to show that these fragile cantilevers magnetic tipped cantilevers are useable in an MRFM experiment.

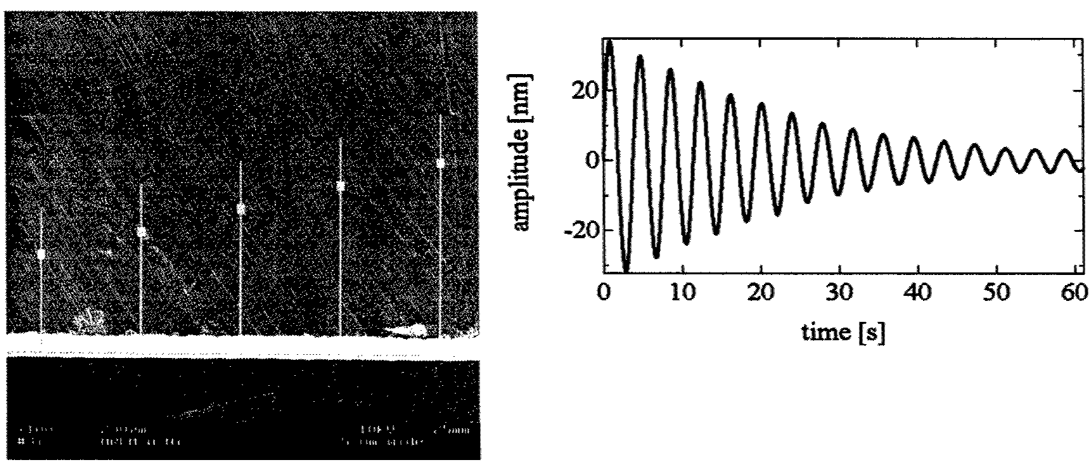


Figure 7. Left: Ultrafloppy silicon cantilevers created at the Cornell Nanofabrication Center. Right: Lock-in demodulated cantilever ringdown transient.

The starting point for the fabrication are the ultrafloppy cantilevers already developed over the last three years by the Marohn group, working in the Nanofabrication Center at Cornell University. Figure 7 shows 340 nm thick single crystal silicon cantilevers, made from silicon-on-insulator wafers, with spring constants as low as a few μN/m. This is approximately four orders of magnitude softer than the best commercially-available silicon-nitride cantilevers which have spring constants ~0.01 N/m.

We began Phase I by examining a number of these cantilevers in detail. The spring constant is measured by following thermomechanical position fluctuations. Cantilever resonance frequency and ringdown time (quality factor) were inferred by driving the cantilever near resonance, demodulating the cantilever oscillations with a lock-in amplifier, watching the demodulated cantilever decay, and fitting the resulting transient to a decaying sinusoid. An example lock-in

demodulated transient decay is shown above. Our best cantilevers take over a minute to ringdown!

One cantilever examined was 400 µm x 7 µm x 340 nm in dimension, with a spring constant of $k = 8.27 \times 10^{-4}$ N/m, a resonance frequency of $f = 2.188$ kHz, and a quality factor of $Q = 182{,}000$ at a temperature of 11 Kelvin. The calculated force sensitivity for this cantilever is $F_{min} = 14$ aN/Hz$^{1/2}$ at 11K. We are only the second group worldwide to achieve such force sensitivity [5]. Our force sensitivity is comparable to the best ever achieved at our operating temperature, which is remarkable since we have employed no heat treatment or surface modification to achieve the observed high quality factor. Our force sensitivity scales to ~ 8 aN in a 1 Hz bandwidth at 4K. conservatively assuming no additional Q improvement (which is expected).

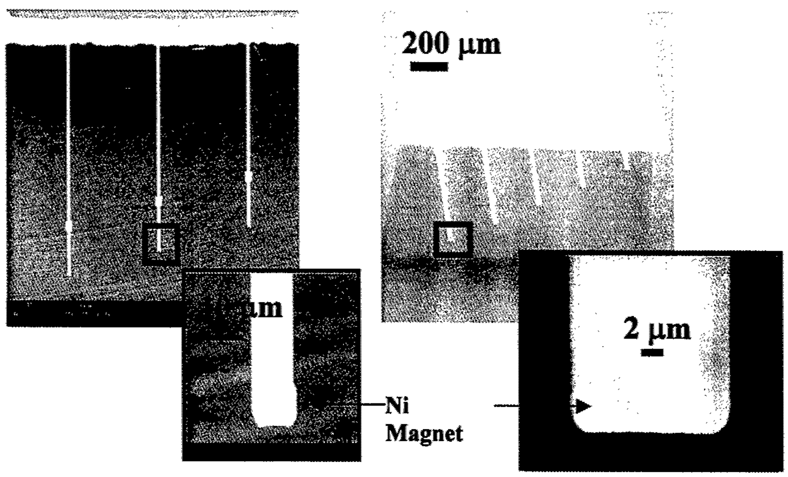


Figure 8. Magnetic tipped ultrafloppy cantilevers, fabricated by lithography, metal evaporation, and liftoff. Left: Large, micron-scale tips patterned by optical lithography. Right: submicron tips by ebeam lithography. The tips shown are composed of nickel.

We deposit nickel and cobalt magnets using the liftoff process. Micron scale magnets can be defined using optical lithography, and we have succeeded in defining submicron magnets using electron beam lithography. Figure 8 (right) shows a 200 nm thick × 400 nm wide × 1200 nm long nickel magnet that we have fabricated by electron beam lithography and lift-off near the tip of one of our custom ultrafloppy cantilevers. We are the first group worldwide to have succeeded in batch fabricating submicron magnets near the tips of attoNewton sensitive cantilevers.

From the shift of the cantilever's resonance frequency versus magnetic field we can learn about the magnetic properties of the submicron magnet at the cantilever tip, using procedures developed by Marohn et al [6] and Stipe et al [7]. Figure 9 (left) the inferred magnetic tip magnetization, which saturates as ~0.3 Tesla, within a factor of two of what is expected for bulk nickel. Stipe has found that the ringdown time of a magnetic tipped cantilever is a function of magnetic field. They have devised a model that allows one to infer the transverse magnetic field fluctuations of the magnet from the measured "magnetic friction." Applying their formalism to the magnetic friction measured for our magnets – see Figure 9 (right) data – we infer that the transverse magnetic field fluctuations produced by our magnets are ~600-800 Bohr magnetons per root Hertz.

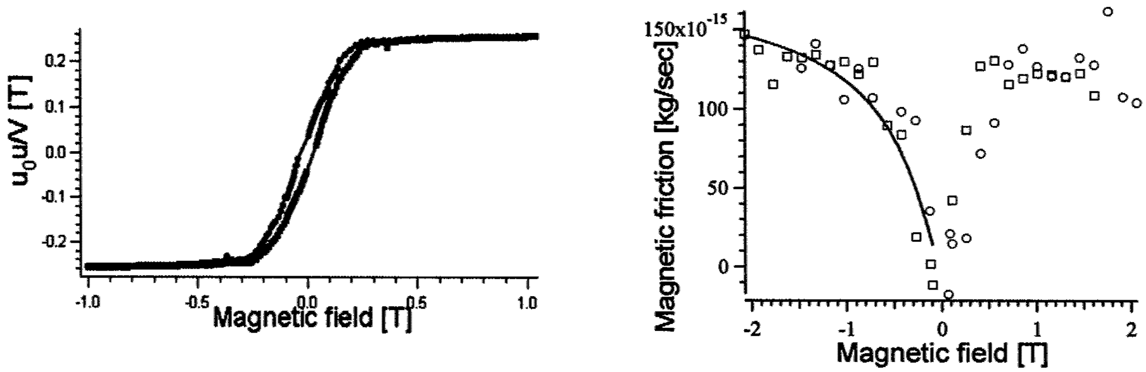


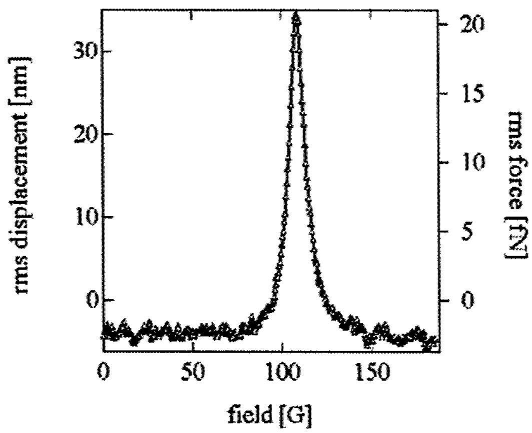
Figure 9. Cantilever frequency shift and ringdown magnetometry studies of a submicron nickel magnet. Left: Measured M-H hysteresis curve. Right: Measured magnetic friction vs. field.

We can say definitively that the fluctuation tip magnetic moments from our submicron magnets will not relax nuclear spins in an MRFM experiment. We estimate that tip field fluctuations lead to a spin-lattice relaxation time for nuclear spins of ~30 seconds, which is acceptable.
These results are extremely exciting. First, while the tip magnetic moment is far too small to measure with a commercial Superconducting Quantum Interference Device (SQUID), we can easily quantify the magnetic moments using frequency-shift magnetometry. Second, the tip magnetic moment comes out roughly as expected for saturated bulk nickel, which shows that our nickel deposition protocol is satisfactory. Third, we can quantify tip magnetization fluctuations and show that they will likely not be a serious additional source of spin-lattice relaxation in NMR measurements. While it is still an open question whether the magentization holds up as we shrink the particles to the single-spin target diameter of ~30 nm, we have established that our cantilever magnetometry is sensitive enough to measure the tip magnetic moment (and fluctuations) for a single nanomagnet.

Interaction of an ultrafloppy cantilever with RF

A possible major concern is that the RF will interact with the magnetic tipped cantilevers. The cantilevers are very thin, and one might worry that they are very sensitive to RF induced heating of the metal tip and so forth. We have carried out control experiments to show that the RF driving the tip (or shifting its resonance frequency) is not a problem.

The figure on the next page (left) shows sample-on-cantilever force-detected electron spin resonance of DPPH at 90 K. The cantilever spring constant was 6 x 10^{-4} N/m, had a resonance frequency of 1.1 kHz, and a quality factor Q of 1000. The cantilever in this case had a magnetic tip, and we simply glued the sample over the top of the tip. The peak at ~110 Gauss is the expected electron spin resonance. The RF in these experiments was amplitude modulated at the cantilever frequency, but only drove the cantilever by an amount equivalent to a few femtoNewtons. This is very promising, and indicates that RF driving of nanoscale magnetic tips will not be a problem.



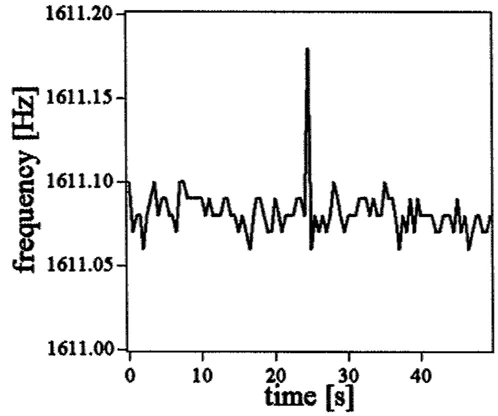


Figure 10. Left: Force detecting electron spin resonance detected by gluing a test sample to a custom magnetic tipped ultrafloppy cantilever. Right: Response of the frequency of a magnetic tipped ultrafloppy cantilever to an intense ~1 Watt of RF irradiation, turned on at ~20 seconds. Both data sets were recorded at a temperature of 77 Kelvin.

The control experiment at the right is an even more exciting result, showing that even a Watt of RF (applied with the PCB board microcoil described in Task 1 above) will not shift the resonance frequency of an ultrafloppy cantilever, if only applied for a few seconds. This is an extremely promising result for spring constant detection of magnetic resonance. In these experiments we excite the cantilever with a capacitive drive wire. The cantilever signal from a fiber interferometer is fed to an analog positive feedback circuit, which in turn drives the cantilever. In this way the cantilever is always self oscillated at its own resonance frequency. The frequency of the resulting self oscillation is detected with a commercial frequency counter. In the above experiment, the frequency fluctuations are within ~5x of what is expected given the drive amplitude and thermomechanical position fluctuations. There is a short transient blip in the cantilever frequency at ~25 seconds when the ~1 Watt of RF is turned on; other than the blip, the cantilever frequency is unaffected by the RF.

The interaction of an ultrafloppy cantilever with a surface

Single-spin MRFM requires that we be able to position an ultrafloppy cantilever within a ~10 nm of a surface. We have used our Phase I MRFM probe (see Task 1 above) to show that we can bring an ultrafloppy cantilever within a few tens of nanometers of a surface and the cantilever will still maintain a good quality factor and force sensitivity.

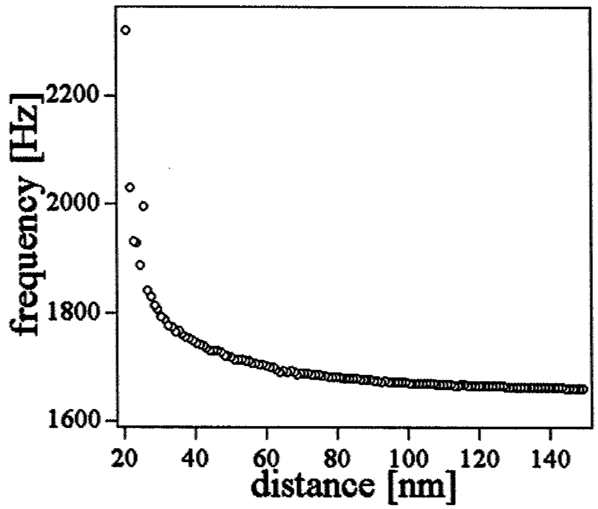


Figure 11. Cantilever frequency as a function of tip-sample separation.

In the above figure we follow the resonance frequency of an ultrafloppy cantilever (spring constant ~100 μN/m) as it approaches a surface. The location of the surface is estimated within +/- 10 nanometers as the distance at which the cantilever stops oscillating. The sample surface in this experiment is polystyrene at 77 Kelvin. The cantilever ringdown time was observed on an oscilloscope at ~10 nanometer intervals. Results (not shown) indicate that a Q in the low thousands is maintained to within ~20 nanometers from the surface. Given the micron-sized tips on our cantilevers, this is already an extremely encouraging result for single-spin NMR. We expect that the cantilever can approach the surface even more closely once we sharpen the tips.

Task 3: A digital-signal-processing based cantilever controller

Task 3 was carried out with the Cornell and SC Solutions teams working in close collaboration. We met once a week in a ~1 hour conference call to discuss weekly progress.

Model-Based Active Control of the Cantilever

Active control of the cantilever is needed for several reasons:

- The cantilever thermomechanical oscillations can be many nanometers. These random oscillations must be damped to far below 0.1 nm rms if atomic-scale imaging resolution is to be achieved.
- A faster damping of the cantilever is needed to increase imaging speed. Cantilevers with a high quality factor have lengthy ringdown time (many 10's of seconds) that slows imaging.
- The cantilever oscillation frequency must be measured continuously, and the spin-modulation reference frequency must be continually readjusted, as the cantilever approaches the surface.
- It is desired to operate the cantilever in two modes, an MRFM mode in which all motion is actively damped away (the "signal" then becomes the control force required to keep the cantilever from *not* moving), and an AFM mode in which the cantilever is driven while amplitude and phase shifts are detected to record an AFM image as the sample is

scanned. We envision that one will "find" a surface feature by AFM and then image underneath it with MRFM.

To develop a robust controller, a model-based control design strategy was used. The model-based approach depends on the development of a physical dynamic model of the system to perform the control design. There are great potential benefits of this approach. For example, the development of a physical model, in cooperation with system designers, provides understanding of what the performance limits are, and what aspects of the MRFM design affect these limits. Also, since the ultimate performance of the system results from the combination of hardware and controller software, there is a big advantage to having a model of both. Another advantage of this approach is that control design can be done in parallel with system re-design if necessary.

Cantilever Physical Model

The simplest form of the dynamics of the cantilever may be represented as a standard second-order flexible system with natural frequency, ω_n, and damping, ζ,

$$m\ddot{x} + b\dot{x} + kx = u$$

where, *m* is the effective mass of the cantilever, the linear damping is represented by *b*, and *k* is the spring constant, *u* is the applied force to the cantilever tip, and *x* is the position of the tip. We may re-write the model in transfer function form,

$$G(s) = \frac{X(s)}{U(s)} = \frac{\omega_n^2}{k(s^2 + 2\xi\omega_n s + \omega_n^2)}$$

where, $\omega_n = \sqrt{\frac{k}{m}}$, and the quality factor is defined as, $Q = \frac{1}{2\xi} = \frac{\sqrt{km}}{b}$ [8].

Cornell uses two types of cantilevers. 1) The Type I cantilever (k = 1 N/m, f = 20-25 kHz, Q = 3 – 5 $\times 10^4$) is commercially available. 2) The Type II cantilever is custom fabricated at Cornell (k = 10^{-2} - 10^{-5} N/m, f = 1 – 12 kHz, Q = 1 – 3 $\times 10^4$). The Type II is cantilever has a nanomagnet attached to the tip and should be suitable for MRFM type experiments.

Figure 12 shows a typical frequency response plot of the Type I cantilever. The high precision levels required in this application, the availability of a very accurate physical model of the cantilever response, and good understanding of the disturbance and noise sources acting on the system make the use of model-based control design techniques a natural choice. Hence, a complete physical model of the system should be derived. For example, we imagine that a more realistic model should include both translational and rotational motion and possibly more than one flexible mode.

Active Control Strategy

As stated previously, a prerequisite for active cantilever control includes the necessity of accurately determining the frequency and amplitude of the cantilever position. These frequency shifts are caused by force gradients from the sample surface acting upon the cantilever tip. The amount of resonance frequency shift measured as the tip passes over the sample can be readily

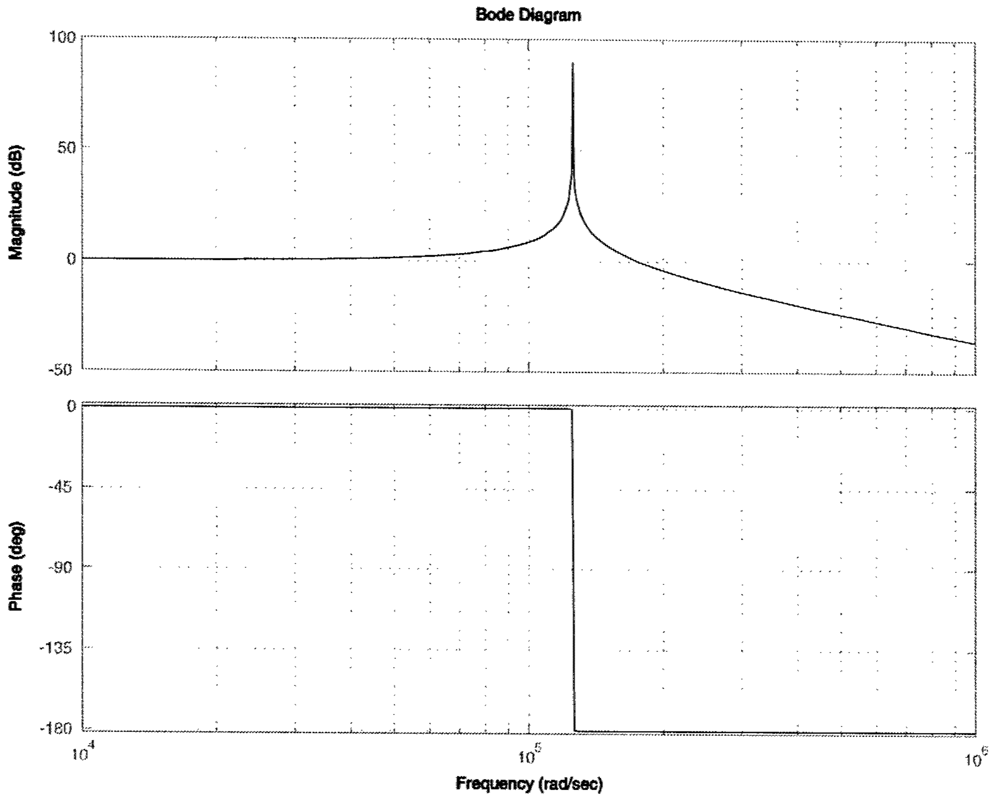


Figure 12. Frequency Response Plot of the Cantilever.

turned into a frequency shift image that quantifies the topography of the surface. Frequency shifts on the order of 10^{-3} Hz must be accurately measured for tips with a resonant frequency of up to ~ 20 kHz. It is also desired to detect these shifts within 10 ms. These specifications require a high degree of hardware and software precision thus making the frequency shift measurement a difficult problem.

Currently, the Marohn group uses the cantilever in a positive feedback loop with a hardware frequency counter to measure the resonance frequency shifts. It is desired to replace this setup with analog I/O boards and a digital signal processor (DSP) for signal processing. Analog I/O boards are provided by Signalware. Target DSP hardware for this implementation is a Texas Instruments TMS320C6701.

Figure 13 shows a block diagram representation of the MRFM system at Cornell. From a control systems point of view there are three loops in the nonlinear closed-loop system. An inner loop will be responsible for maintaining the cantilever at its resonance frequency. The amplitude of cantilever oscillation can be placed under closed-loop control. Also, the "z" distance between the sample and the tip is also suitable for closed loop performance enhancement. The amplitude and "z" distance controllers can be considered as outer loops where cantilever amplitude and sample to tip distance are controlled to maximize performance. Control of these quantities will also allow for improved disturbance rejection thus decreasing the time necessary to obtain an image.

There are also various control problems to solve in addition to the signal processing mentioned above. We anticipate using the simulation of the MRFM system augmented with sensor/process noise characterization (from the real system) as an aid in designing these controllers. Future directions in MRFM control might allow for development of a multi-input multi-output (MIMO) controller that incorporates all of these single loops into one controller.

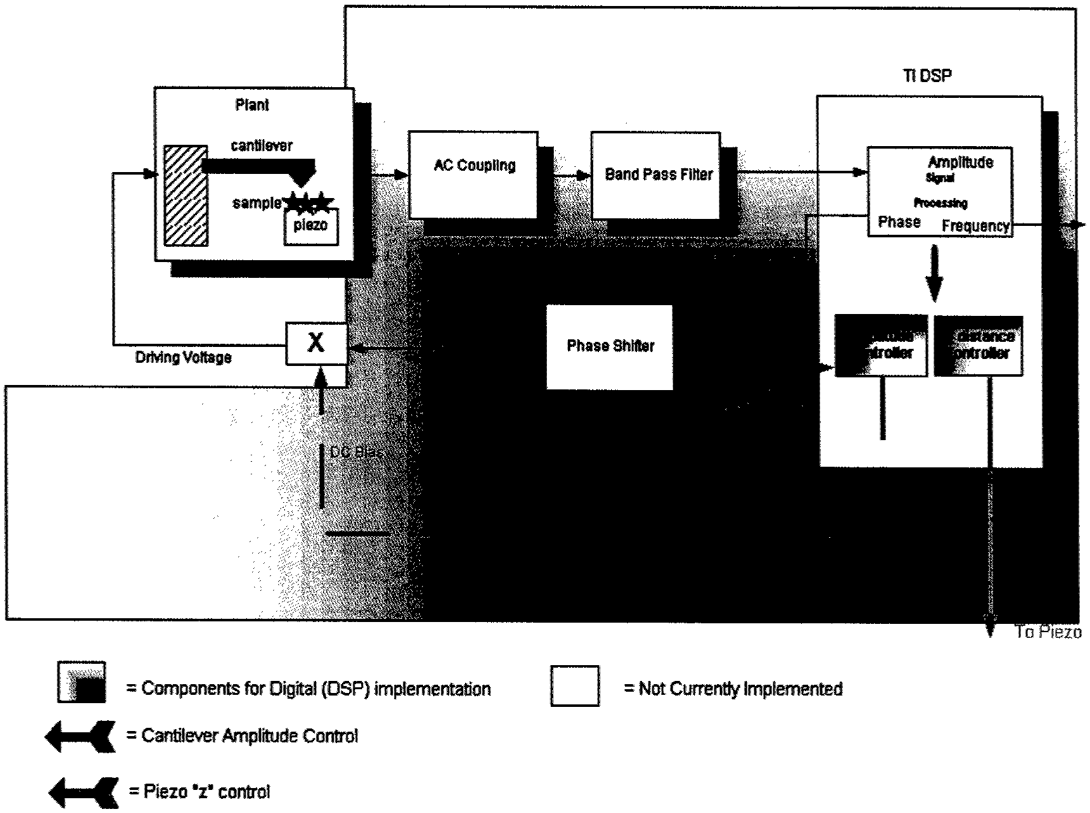


Figure 13. **Schematic Block Diagram of the MRFM Closed-loop System.**

In particular, the Cornell group has indicated that the hardware will require three analog outputs and one analog input. The analog input will be the cantilever position measured by interferometer. The digital signal processor (DSP) will be responsible for calculating and sending three outputs to the analog output daughter card: 1) A voltage proportional to the instantaneous frequency, 2) Voltage signal to the piezo base which will be used to drive the cantilever, and 3) Signal to the control the vertical displacement between the cantilever and the sample.

Doran Smith of ARL agreed to loan SC a duplicate copy of his hardware, which consists of a Texas Instruments' Evaluation Board Module C6711 along with one daughter board (manufactured by Signalware, Inc.) for input and output. Ultimately, the daughter card will be driven by an external reference, however, the current loaned copy has an on-board clock. Extremely stable external clock sources (i.e., 7ppb at 0 – 55°C) are available. The TI evaluation board is currently limited by an on board clock with a stability of approximately 100 ppm. This amount of jitter is unsuitable for performing measurements in the mHz range. Therefore our implementation must allow for the input, calculation, and output to be suitably synchronized.

Various methods for measuring the frequency shift have been investigated. These techniques include:

1) Using a phase-locked loop (PLL) in a positive feedback scheme such that the PLL output locks on to the input signal. The resonant frequency shift due to sample/cantilever interaction is available as well as a "clean" sinusoidal version of the signal that can be used to excite the cantilever. Internal PLL signals can be low passed to form a signal proportional to the estimated frequency. The "clean" sinusoidal version (VCO output) can also be used to estimate the input signal's frequency.

2) Computing the 2-norm of the error between the input signal and sine-waves of known frequency, amplitude, and phase over a given time interval (e.g., 10 ms of data). Minimizing this error yields an estimation of the input signal's characteristics.

3) Adaptive frequency estimation scheme as described in reference [9]. This technique allows for estimation of the fundamental frequency as well as higher harmonics. It is very similar in nature to the PLL. A distinct advantage of this method is that the phase, magnitude, and frequency are simultaneously estimated.

Methods 1 and 2 were found to be unsuitable for DSP implementation given the high accuracy required. In using method 1 we had hoped to use a software implementation of a PLL and low pass certain signal components to obtain the signal's frequency, magnitude and phase (See Figure 14). Using the PLL should give a nice result as the frequency and phase of the input signal are very effectively tracked.

We found that the PLL can be an effective technique if the phase-lock loop is implemented in hardware [10] (e.g., J-K Flip flops, counters, and highly stable oscillators), however, the code required to implement a PLL in software is not fast enough on a DSP for the required measurement accuracy. Cornell would like to be able to resolve shifts on the order of 1 – 10 mHz in approximately 10ms.

Cornell was able to provide data where frequency shifts of 5, 10, 30, 70, and 100 mHz were performed. Shifts of 30 and above were detectable while the shifts of 5 and 10 mHz were not. One reason for this detection failure of small shifts is due to the noise in the system. Figure 15 shows a typical plot of the noise characteristics. One method of obtaining a frequency estimate is to low pass the input to the PLL's voltage control output (VCO). Figure 16 shows some results of using the PLL scheme (only showing 5, 10, 30 and 70mHz shifts). The large amount of noise at low frequencies severely hampers this method. In addition, the signal computed by this method is proportional to frequency and a suitable scaling must be found - thus there may be calibration issues. An alternative method of estimating the signal frequency is to use the VCO signal (which is a clean, filtered version of the cantilever input signal) and estimate its frequency.

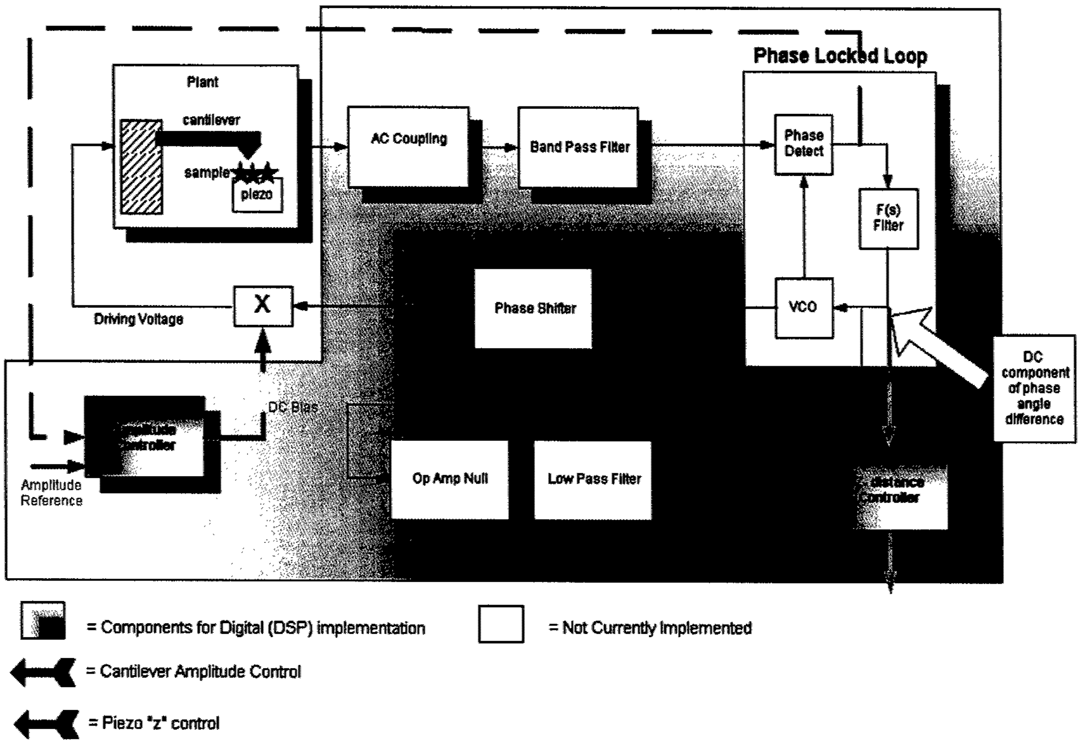


Figure 14. Using the PLL in a Closed-loop Scheme.

Using a simple batch method to compute the frequency (count the number of zero crossings in a fixed interval of time – basic principle of the hardware frequency counters), the PLL would need to run at approximately 100 MHz in order to resolve a 5 mHz frequency shift within 100ms. 100Mhz sampling of the cantilever signal will yield 2200 zero crossings in 100ms. The ability to resolve the difference between resolving 22 kHz and 22.000005 kHz with 2200 points will require eight digits of precision. In order to resolve shifts on the 10ms timescale, which is the goal, we had to investigate more optimal methods of determining the frequency. Figure 17 and Figure 18 show some sample performance of Method 3 using a clean input signal as well as real data from the Cornell lab that has been bandpassed by a software filter around the resonance frequency. The signal frequency is directly estimated in the appropriate units (i.e., hertz). No additional scaling is necessary. Note the signal is still quite noisy. It is clear that the effect of noise is to degrade the ability of the algorithm to accurately detect frequency shifts. Regardless of the method used, noise will need to be filtered out by analog hardware. When the Cornell equipment becomes functional, we will suggest using a hardware analog filter to reduce the signal noise.

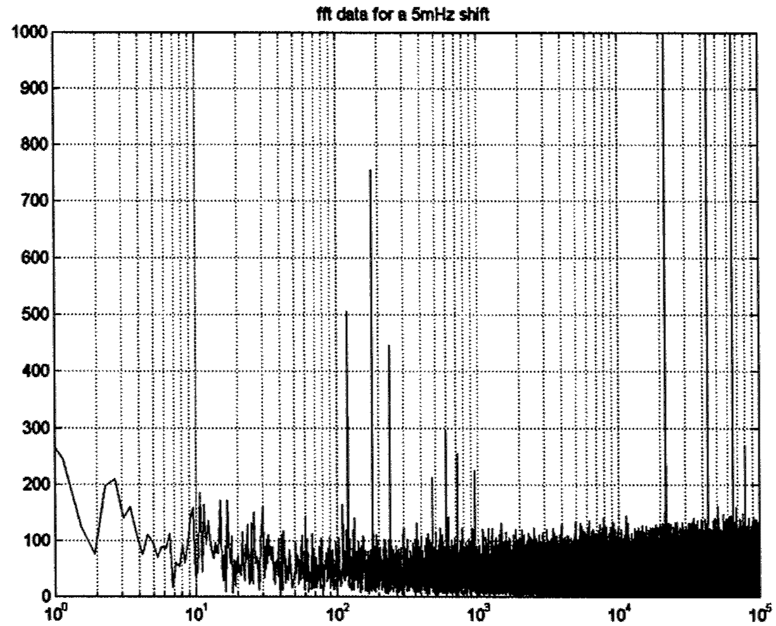


Figure 15. Typical Fast Fourier Transform (FFT) Plot of Noise Characteristics.

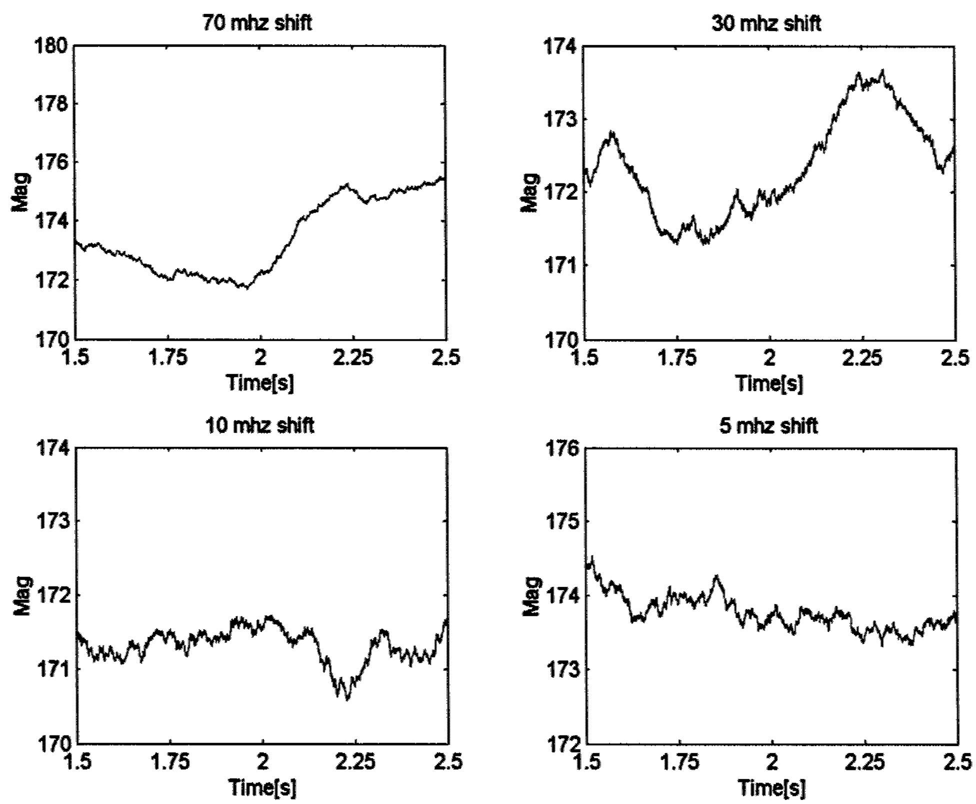


Figure 16. Cornell Data. PLL with Low Pass Method.

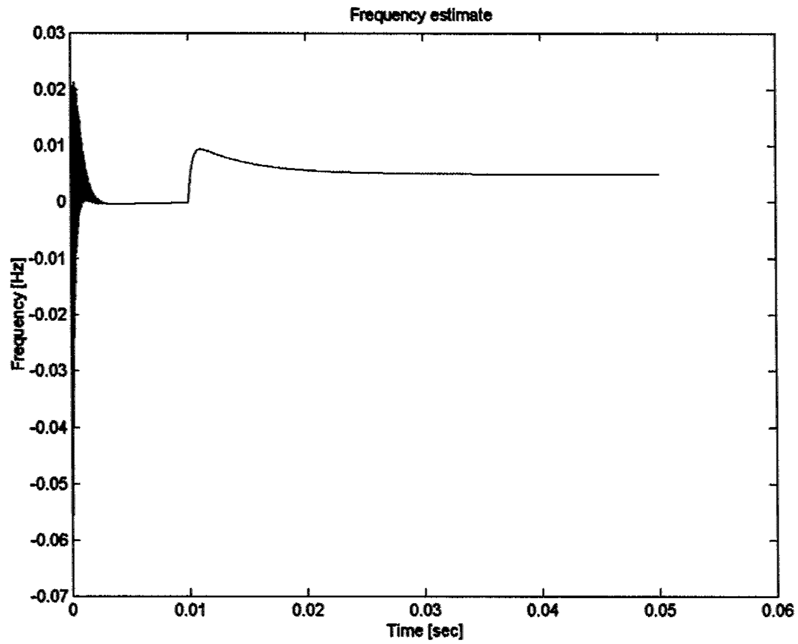


Figure 17. Simulated Data 5 mHz Shift at t = 0.01.

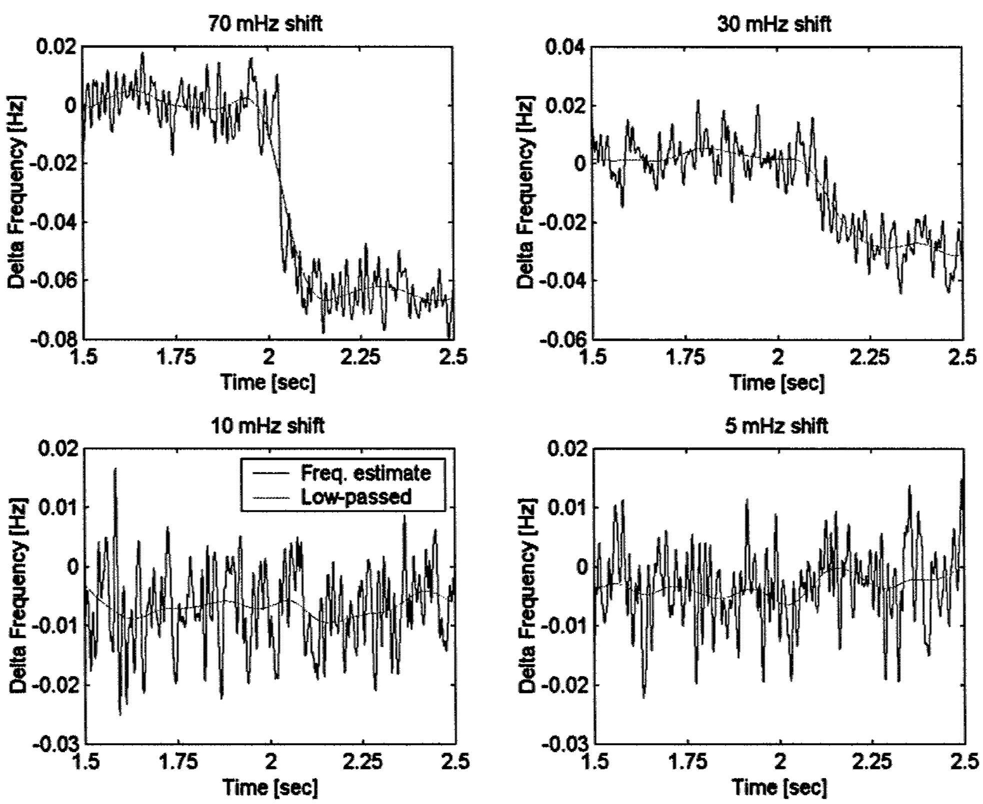


Figure 18. Cornell Data for different shifts at ~ 2 seconds.

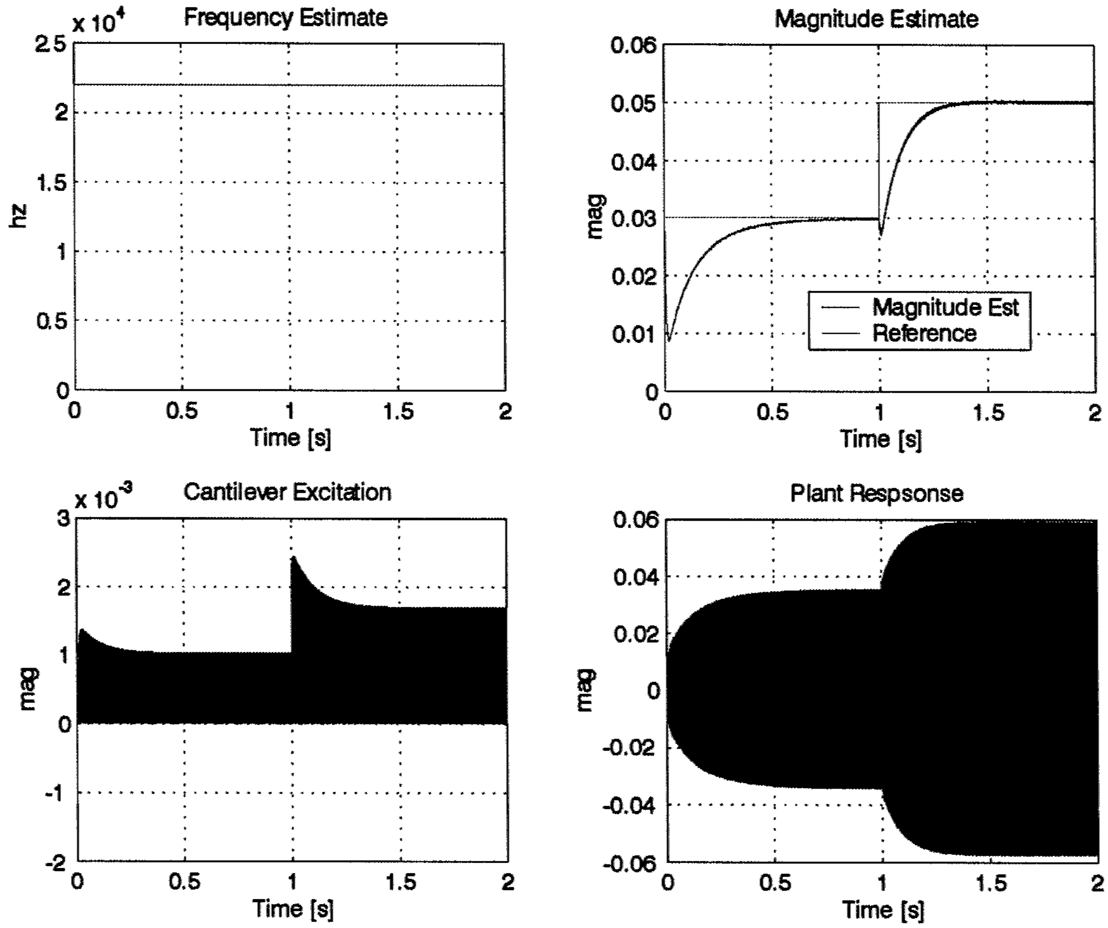


Figure 19. Closed-Loop Amplitude Control Response.

Closed-Loop Control Performance

In simulation, we were able to show closed-loop amplitude control as pictured in Figure 13. Figure 19 shows sample close-loop control results. The preliminary controller here is a simple proportional integral (PI) controller [8]. We fully expect that as we develop a better understanding of the system and noise characteristics, more advanced control strategies will provide better performance.

Implementation on the TI DSP

We were able to successfully place the adaptive algorithm on our Texas Instruments' DSP Starter Kit (DSK) and loaner hardware (TI DSP Evaluation Module, EVM). The algorithm performs similarly to the simulations above. This is expected behavior as the C-code is essentially the same. The Code Composer IDE provides tools for profiling the real-time execution of the code. Currently on the TMS320C6711 DSP (runs at 150 MHz on the DSK & EVM) the frequency estimation algorithm requires approximately 13-16 μs to complete. For the signal range of ultrafloppy to stiff cantilever (i.e., 1 KHz to 22 KHz) this time should be sufficient to provide accurate frequency measurements and have time to do some control of amplitude/z-distance; however, we will investigate ways to reduce the algorithm execution time. One possible method

of reducing the computational time is to place the algorithm on the daughter board's FPGA. The FPGA is capable of performing calculations much faster than the TI DSP. We also made some investigation into connecting the DSP to the external world (i.e., analog inputs and outputs). Actual implementation with analog I/O will require some clock synchronization (the DSP and analog I/O board will run on separate clocks) but our cursory examination and testing of the I/O board with DSP shows that the integration is quite feasible.

Task 4: Single spin feasibility

In our Phase I proposal we presented an estimate of what would be required to detect a single electron and a single proton by magnetic resonance force microscopy. Here we briefly consider the size of the signal from a single proton in a spring constant detection experiment.

Rugar *et al.* have approached a surface within h = 5 nm using an ultrafloppy cantilever [7]. The optimal diameter magnetic particle for spring constant detection has diameter $3h = 15$ nm which is at the lower limit of what can be defined by electron beam lithography. The spring constant change due to a single proton is $k_p = 1.5 \times 10^{-10}$ N/m. This would be measurable if we employ a cantilever capable of detecting a force of 10^{-18} N and oscillate it to a $x_{0p} = 10$ nm amplitude, for which $\delta k_{min} = 10^{-10}$ N/m in a 1 Hz bandwidth.

Although further optimization needs to be done, we have demonstrated through our Phase I STTR experiments that it is entirely feasible to construct the hardware required to detect a few thousand protons. *We believe that it will be possible to push cantilever-detected magnetic resonance to single proton sensitivity by optimizing the hardware and protocols already demonstrated in our Phase I work.* We can build the cryogenic coarse approach and pulsed RF hardware, we can make the required cantilevers, get them close to a surface while maintaining sensitivity, and can construct a DSP controller to readout cantilever frequency and/or damp cantilever thermal motion.

Results Obtained

The main objective of our Phase I proposal has been achieved. We have developed a commercially feasible design for a magnetic resonance force microscope capable of detecting a few thousand nuclear spins, and have carried out experiments to show that building such an instrument is feasible.

We are the first group to fabricate attoNewton-sensitive cantilevers with nanomagnet tips. We have shown with our Phase I cryogenic microscope that it is possible to bring an ultrafloppy cantilever close to a surface while maintaining force sensitivity. We have demonstrated that magnetization fluctuations in the nanomagnetic tips will not seriously degrade sample nuclear spin-lattice relaxation times, and that the magnetic tipped cantilevers are immune to spurious driving by RF.

In light of Cornell's advantageous proposal for detecting NMR as a cantilever frequency shift, the team devoted most of its effort to the challenging task of measuring milliHertz cantilever frequency shifts using versatile DSP technology. Such accurate frequency shift measurement is in fact a prerequisite to providing cantilever control of thermomechanical position fluctuations as well. We have demonstrated that it will be feasible to construct DSP hardware that can simultaneously measure small transient shifts in cantilever resonance frequency and also be capable of actively damp cantilever fluctuations during image encoding.

We found the problem of simultaneous estimation of the frequency and phase, at the required precision, to be rather challenging. We investigated a number of methods of frequency estimation in detail. The PLL method was not found to be suitable on a DSP given the performance specifications. The adaptive frequency estimation technique has shown the most promise for detecting small frequency shifts in a short amount of time. The adaptive frequency estimate does not require as much computational complexity and it estimates the signals frequency, phase, and magnitude. Additionally, we demonstrated feasibility of closed-loop amplitude control using a preliminary feedback controller. The software was executed on a DSP to demonstrate feasibility of the embedded control implementation.

In summary, all the proposed Phase I tasks have been demonstrated, proving that it is feasible to construct a commercially viable cryogenic magnetic resonance force microscope capable to detecting and imaging a few thousand protons. The next critical step in the product development process is for the team to carry out a Phase II effort to apply their proven technology to develop a high performance MRFM system. Given our Phase I successes, we are confident that a Phase II development effort will lead to a commercial prototype.

Acknowledgement

STTR funds were used primarily to accomplish the most challenging and novel task described in this report, Task 3, developing a digital-signal-processor-based feedback controller suitable for magnetic resonance force microscopy. In addition to STTR support, our team was able to leverage non-STTR funds from the Army Research Office and the National Science Foundation to cover graduate student wages and thereby make faster-than-expected progress on Task 1 (scanning microscope) and Task 2 (nanomagnetic tipped cantilevers). The additional sources of funding were from the following two grants.

- "Quantum Computing Using Self-Assembled Molecular Spin Arrays," Army Research Office Experimental and Theoretical Development of Quantum Computers Program (P.I. Dave Allara at Penn State), $1,498,600 (total), $434,800 (Marohn), 04/01/02 - 03/31/05 (3 years). Funds two full-time graduate students to advance the state-of-the-art in magnetic resonance force microscope technology and assay spin-spin couplings in monolayer –thick films by electron spin and nuclear magnetic resonance force microscopy.

- "Monolayer nuclear magnetic resonance of organic electronic materials by cantilever detection," National Science Foundation Science and Engineering Center (P.I. Bob Buhrman at Cornell), $55,000, 9/1/02-9/1/03 (1 year), renewable up to four more years. Funds one full-time graduate student to develop a magnetic resonance force microscope tailored for various applications. This year's goal is to detect nuclear magnetic resonance from a single monolayer.

Having these funds available to leverage the STTR investment has greatly accelerated our efforts towards Phase II commercialization of a microscope capable of detecting and imaging nuclear magnetic resonance from a few thousand protons.

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